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TRANSFERENCE NUMBER MEASUREMENTS FOR THE POLYMER ELECTROLYTE P0--ETC(U)

JAN 81 R DUPON, D H WHITMORE, D F SHRIVER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Fmf measurements have been determined in a Na/Hg amalgam concentration cell containing the solid electrolyte poly(ethylene oxide)-NaSCN. These results in conjunction with measurements made with blocking electrodes of the frequency dependent conductivity, demonstrate that the main charge carrier is Na <sup>+</sup> .		

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## Transference Number Measurements for the Polymer

### Electrolyte Poly(ethylene oxide)·NaSCN

R. Dupon, D. H. Whitmore, and D. F. Shriver  
Departments of Chemistry and Materials Sciences, and  
Materials Research Center, Northwestern University  
Evanston, Illinois 60201

Current interest in the development of high energy density batteries has focused considerable attention on solid electrolytes. The leading solid electrolytes in developmental batteries are hard ceramic materials, which usually are employed at elevated temperatures with liquid electrodes. A more compliant solid electrolyte, such as a polymer electrolyte, should enable contact to be maintained at the electrode-electrolyte interfaces in an all solid state battery and lower operating temperatures might be facilitated. Potential application of ion-containing polymers as battery electrolytes, and electrical measurements on salt complexes with poly(ethylene oxide) and with poly(propylene oxide) have been presented by Armand (1,2), and structural studies of poly(ethylene oxide) salt complexes have been reported from our laboratory (3). The original synthesis and characterization of these materials was reported by Wright (4,5) and extended by James (6).

A fundamental parameter in the characterization of any solid electrolytes is the fraction of the total current which is carried by the mobile ion, i.e. the transference number. Prior to the present work, a rigorous determination of the transference number for poly(ethylene oxide) based electrolytes was not available. The present study is based on the measurement of emf between ion reversible amalgam electrodes which are separated by the solid electrolyte in a concentration cell (7,8).

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**Key words:** Solid electrolyte, polymer electrolyte, transference number, poly(ethylene oxide).

## EXPERIMENTAL

Poly(ethylene oxide) with an average molecular weight 600,000 was obtained from Aldrich. The polymer was purified by ion-exchange of an aqueous solution and the solvent was subsequently removed under high vacuum. Reagent grade NaSCN (B & A) was recrystallized from methanol and dried under high vacuum. Reagent grade methanol (MCB) was dried by distillation from iodine-activated magnesium under a nitrogen atmosphere.

A PEO·NaSCN complex, 4.5:1 mole ratio of polymer repeat unit to salt, was prepared from stoichiometric quantities of the polymer and salt in anhydrous methanol. Following complete dissolution of the two solids, the methanol was removed under vacuum. All manipulations were carried out using standard inert atmosphere techniques (9). The identity of the PEO·NaSCN complex was confirmed by infrared spectroscopy and differential scanning calorimetry, and in previous research the material prepared by this same procedure has been characterized by optical microscopy and x-ray diffraction, which demonstrate the absence of free NaSCN.

Amalgams were prepared with triple distilled mercury and reagent grade sodium (MCB). Molten sodium was filtered through fritted glass to remove sodium oxide. The concentration of the stock amalgam, solution No. 1, Table I, was determined gravimetrically and checked by the gasometric method based on the amount of hydrogen evolved from the reaction of the sodium amalgam with hydrochloric acid. Concentrations of the remaining solutions were determined gravimetrically by successive dilution of the stock amalgam. X

The sample and amalgams were placed in a cell which permitted exclusion of the atmosphere, Fig. 1. A pressed pellet of the PEO·NaSCN complex, 4.5:1, was fitted into an o-ring which was then clamped between the side arms. All loading of the polymer complex was carried out in a nitrogen

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filled dry box. One side arm was filled with the stock amalgam solution while the other was successively filled with the dilutions of the stock. Introduction of amalgam solutions was done with a gas-tight syringe under a flush of dry nitrogen.

The potentials of the cell were measured using a Keithley 177 multimeter together with an electrometer containing an RCA CA3140 E MOS/FET operational amplifier designed to increase the input impedance of the measuring device to  $10^{12}$  ohms. All measurements were made at room temperature,  $23.5 \pm 0.2$  °C, which was monitored using an iron-constantan thermocouple and millivolt meter. The cell and connecting leads were placed in an aluminum box designed to shield the system from extraneous radiation. Reversing the cell polarity produced insignificant changes in the magnitude of the observed potentials. The emf was read after the potential had maintained a stable ( $\pm 0.3$  mV) value over a period of one hour. Typical stabilization times were of the order of one to two hours. The measured results are given in Table I. As a check on these measurements, emf values were determined on a different batch of the polymer electrolyte using different amalgam preparations. Agreement between the data sets was good.

A value of the cell impedance was obtained by loading standard resistors in parallel with the cell and observing the change in emf. The observed room temperature cell impedance of  $3.9 \times 10^6 \Omega$  was well within the capability of the measuring device and yielded a D.C. conductivity of  $6.3 \times 10^{-8} (\Omega \text{ cm})^{-1}$ , which is in general agreement with the A.C. value shown by Armand (2).

The emf of the concentration cell  $\text{Hg-Na}(x_1) \mid \text{PEO} \cdot \text{NaSCN} \mid \text{Hg-Na}(x_2)$  is expressed by (8):

$$E_{\text{obs}} = (1 - t_e)E_{\text{id}} = (1 - t_e) \frac{RT}{nF} \ln \frac{a_1}{a_2} = (1 - t_e) \frac{RT}{nF} \ln \frac{\gamma_1 x_1}{\gamma_2 x_2}$$

The activity coefficients for dilute amalgams (present case) may be calculated from the relationship (10):

$$\log \gamma = Qx$$

where

$$Q = 18.720 - 8.00 \times 10^{-3} T$$

From this,  $E_{\text{id}}$  may be calculated:

$$E_{\text{id}} = \frac{RT}{F} 2.303 \log \frac{x_1}{x_2} + \frac{RT}{F} 2.303 Q(x_1 - x_2)$$

A plot of  $E_{\text{obs}}$  vs.  $E_{\text{id}}$  for each  $x_2$  ( $x_1$  being fixed as the stock amalgam, solution No. 1) yields a straight line (Fig. 2) of slope  $(1-t_e)$ .

#### DISCUSSION

For a purely ionic conductor the value of  $(1 - t_e)$  should be unity. Least squares treatment of  $E_{\text{obs}}$  vs.  $E_{\text{id}}$  produced a line of slope  $1.005 \pm 0.005$ , Fig. 2. This result establishes that the electronic contribution to the total electrical conductivity of  $\text{PEO} \cdot \text{NaSCN}$  is negligible and that the ionic component is responsible for the conduction. Since sodium-reversible electrodes were employed and since the conductivity is close to the published ac data, the sodium ion is implicated as the major charge <sup>carrier</sup> in the  $\text{PEO} \cdot \text{NaSCN}$  complex.

Definition of variables:

$E_{obs}$  = the measured emf

$t_e$  = electronic transference number

$E_{id}$  = ideal emf, value of  $E_{obs}$  when  $t_e = 0$

$R$  = universal gas constant

$T$  = absolute temperature

$n$  = number of electrons transferred

$F$  = Faraday constant

$a_1, a_2$  = activities of sodium in the amalgams

$\gamma_1, \gamma_2$  = activity coefficients of sodium in the amalgams

$x_1, x_2$  = mole fractions of sodium in the amalgams

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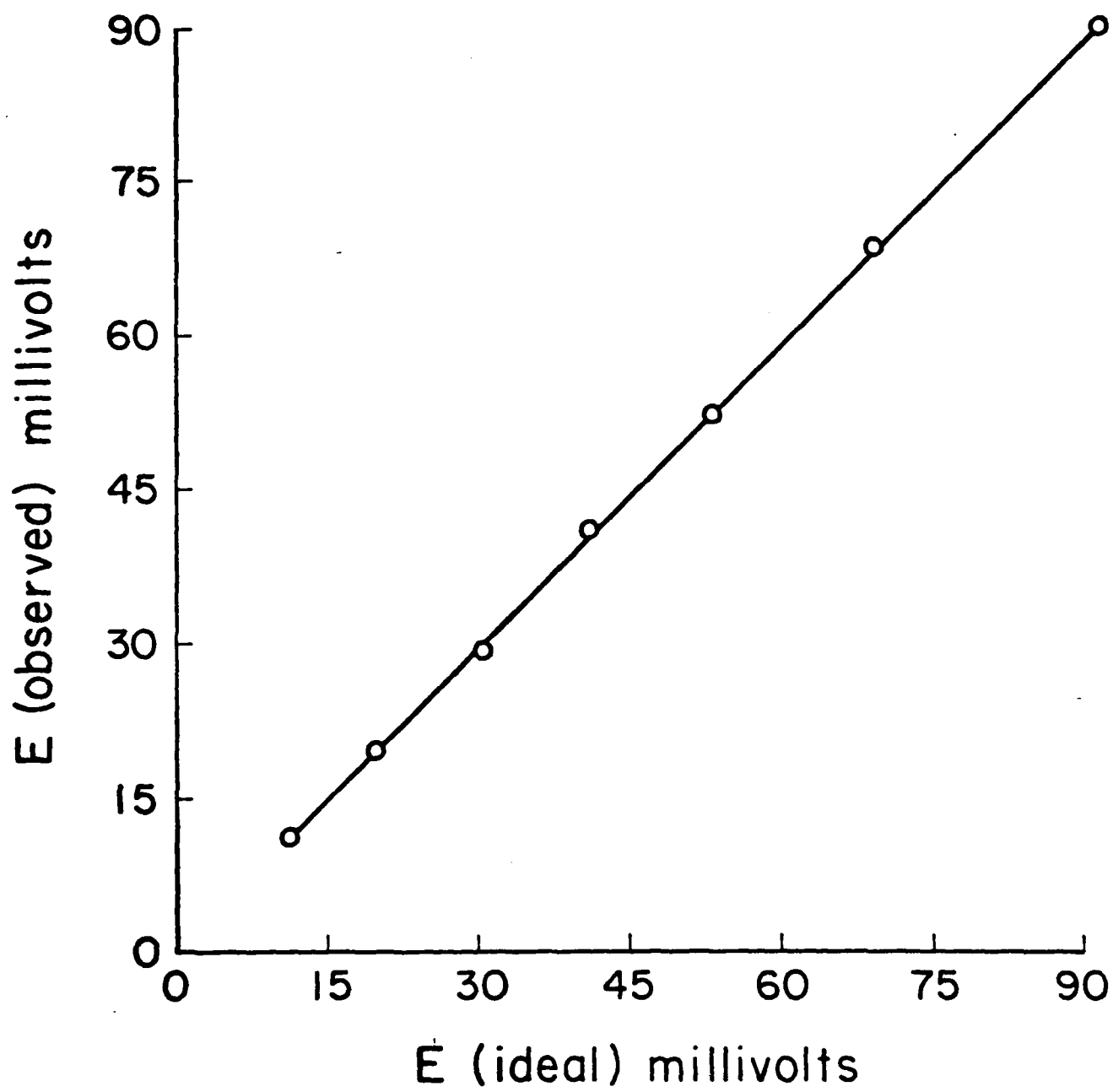
Table I. Ideal and observed emf's of concentration cell at room temperature.

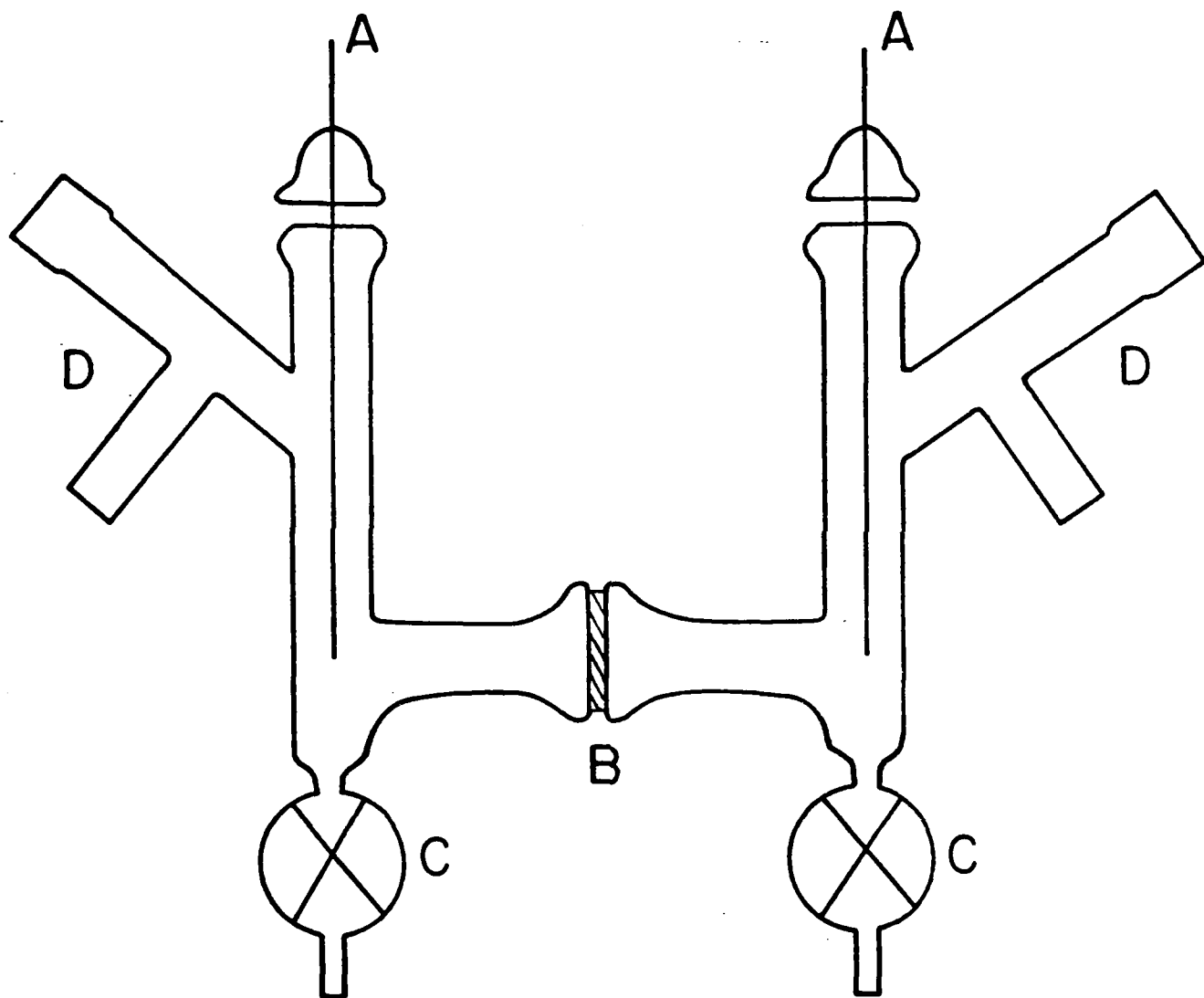
Solution No.	$x_{Na}$	$E_{id}$ (mV)	$E_{obs}$ (mV)
1	0.04103	-	-
2	0.03426	11.13	10.98
3	0.02944	19.64	19.47
4	0.02406	29.99	29.11
5	0.01928	40.25	40.89
6	0.01440	52.36	52.10
7	0.009477	67.84	68.34
8	0.004753	90.00	89.83

FIGURE LEGENDS

Figure 1. Cell for transference number measurements. A, nickel electrode; B, polymer electrolyte; C, stopcock; D, teflon in glass valves for  $N_2$  inlet.

Figure 2. Observed vs. ideal emf values for a Na/Hg concentration cell with NaSCN·PEO polymer electrolyte.





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